

# Comparison of Water Vapor Sorption by Milk Powder Components

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## Abstract

Water vapor is absorbed by milk powder at sites dependent upon the relative pressure,  $P/P_0$ , of the atmosphere to which the powder is exposed. Comparison of the water sorption isotherms for the protein, sugar, and mixed salts comparable with that found in milk powder indicated that at low  $P/P_0$  water is bound primarily by the casein fraction in the powder. As the  $P/P_0$  progresses toward 0.5, lactose becomes more active in water binding. At  $P/P_0 = 0.5$  the lactose accumulates sufficient water to undergo transition from the glass to crystalline hydrate state. This phase transition is accompanied by a net loss of water by the powder and as the relative pressure rises above 0.5, the salts rapidly absorb moisture.

It is widely accepted that the excessive sorption of water vapor by many types of dehydrated foods adversely affects the storage life of such materials, and accordingly a number of reports have been made concerning the absorption of water by dried foods (7). The extent of water binding by individual food components has, however, not been as widely studied as the absorption of water vapor by the foods themselves. Such information should prove useful in developing an understanding of the mechanisms of water binding in the complex systems so characteristic of dried materials of biological origin.

Milk powder is such a complex system wherein water sorption may involve protein, carbohydrate, and mineral fractions, with the probability that one or more of these individual interactions may be responsible for some of the deleterious changes observed in milk powders upon exposure to humid atmospheres (4, 5, 11). We have, therefore, studied the manner in which water vapor is absorbed by isolated milk sugar, salt, and protein fractions and we are here reporting the results of this research.

## Materials and Methods

Sorption studies were conducted on dehydrated samples of the major components of milk,

i.e., lyophilized samples of casein, whey, a synthetic milk salt mixture, lactose, and lactose-free milk. Data for water absorption by lyophilized skimmilk were also obtained to serve as a basis for comparison with the data for the components.

Casein was prepared both by acid precipitation and by centrifugation methods. Acid casein was obtained by precipitation from skimmilk with 1 N HCl to pH 4.7 at 30 C. The crude casein, as obtained from 300 ml of skimmilk, was washed with four 80-ml aliquots of 0.1 N HCl. The washed casein was dispersed in 150 ml of distilled water, titrated to pH 7.0 with NaOH, and dried by lyophilization. Casein was obtained by high-speed centrifugation of warmed skimmilk (30 C) for 30 min at 78,400 g. The casein was washed three times with warm distilled water, and after dispersion overnight in 500 ml of cold distilled water (5 C), the casein was dried by lyophilization.

Total mineral content of the caseins was determined by ashing at 550-600 C. Calcium content was determined by a modification of the method of Murthy and Rhea (8), using the Perkin-Elmer Model 290B atomic absorption spectrophotometer.

The acid whey was filtered and also lyophilized to be used as a sorbent in the sorption studies.

Lactose-free milk was prepared by repeated dialysis of skimmilk against a solution designed to have the salt composition of milk ultrafiltrate (6). Amorphous lactose was obtained by lyophilization of an aqueous lactose solution. An approximation of anhydrous milk salts was prepared for sorption studies by lyophilization of the synthetic milk ultrafiltrate, prepared according to the formula of Jenness and Koops (6).

Before measuring the water absorption, the powders were further dried under high vacuum. This outgassing procedure was considered complete when the powder mass remained constant for several hours at  $10^{-6}$  torr. Moisture removed from the sorbents in this manner was in agreement with results obtained from toluene distillation of the lyophilized materials.

Water vapor sorption at 24.5 C was determined gravimetrically, using the Cahn RG re-

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ording electrobalance<sup>1</sup> incorporated into a glass absorption apparatus equipped with suitable accessories for outgassing the powders and controlling and monitoring temperature and water vapor pressure. The apparatus and experimental technique have been described (1).

## Results

Sorption isotherms for water vapor on lactose-free milk and on lyophilized skimmilk are shown in Fig. 1. The isotherm obtained with the lactose-free milk powder is a smooth, sigmoid Type II isotherm according to the classification of Brunauer et al. (2). The curve for the lyophilized skimmilk, however, shows a decided break at a relative pressure,  $P/P_0$ , of 0.5, in agreement with results obtained previously with spray-dried skimmilk powders (1).

Data for water sorption by lactose are shown in Fig. 2. During the initial segment of this isotherm, until 0.25  $P_0$ , there is relatively little uptake of water. However, after this point the lactose becomes more active in sorption and absorbs water rapidly until 0.35  $P_0$ , where the sample reaches a maximum in mass absorbed. After the maximum there is a sharp loss in weight as water is desorbed at constant relative humidity. Beyond this point the lactose becomes nonhygroscopic with very little sorption occurring, even at  $P/P_0 > 0.8$ .

Data for water sorption by the Jenness-Koops salt mixture are shown in Fig. 3. This isotherm was unique when compared with those obtained for all the other sorbents. It may actually be considered as a Type III isotherm

<sup>1</sup> Mention of brand or firm names does not constitute an endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

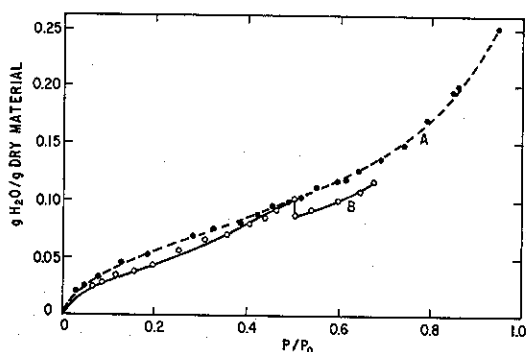


FIG. 1. Effect of lactose content on water sorption isotherms. A, Lactose-free skimmilk powder; B, lyophilized skimmilk.

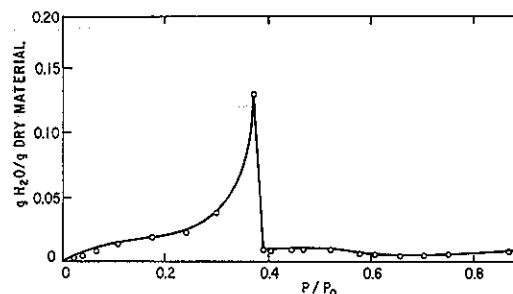


FIG. 2. Water sorption isotherm for freeze-dried lactose.

according to the classification scheme of Brunauer et al. (2). There was essentially no water uptake at pressures less than 0.5  $P_0$ . However, after 0.5  $P_0$  there was very extensive sorption of water. Of all the materials we have studied, the salts were the most hygroscopic, imbibing almost twice their weight in water at 0.95  $P_0$ . There is a break in the isotherm at 0.77  $P_0$  which probably corresponds to a phase change involving crystalline forms of one or more of the salts.

The sorption isotherms obtained with the whey and casein samples are shown in Fig. 4. The whey isotherm is similar in shape to that observed with the freeze-dried skimmilk, except that in the earlier portion of the isotherm there is substantially more water sorbed by the milk powders. The mass sorbed by the whey in this initial segment of the isotherm, up to  $P/P_0 = 0.25$ , is comparable to that observed with pure lactose, which is reasonable, in that whey powders are usually on the order of 70% lactose.

Both acid-precipitated and centrifuged casein yielded almost identical isotherms up to

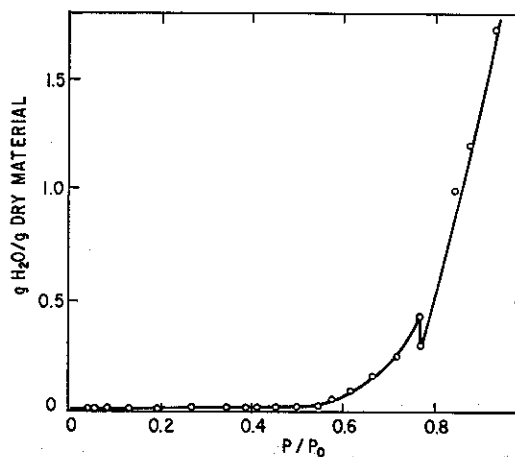


FIG. 3. Water sorption isotherm for anhydrous Jenness-Koops salt mixture.

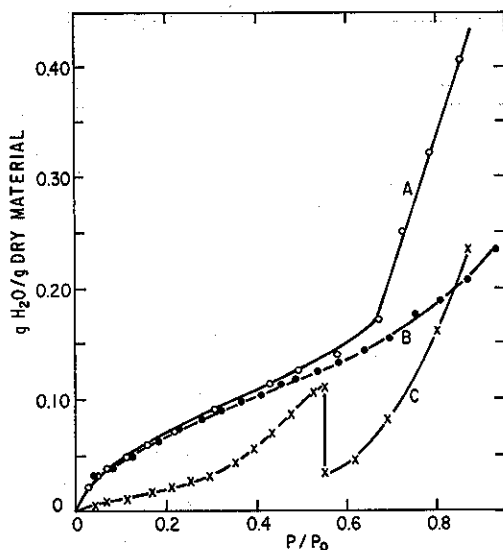


FIG. 4. Water sorption isotherms for powders: A, acid-precipitated casein; B, centrifuged casein; C, acid whey.

$P/P_0 = 0.6$ , beyond which the acid-precipitated casein sorbed far more water than the centrifuged casein. It is unlikely that this difference in absorption capacity is related to the total mineral content of the caseins, as the acid-precipitated and centrifuged caseins, respectively, exhibited ash contents of 7.74 and 7.49%. The caseins did, however, differ in calcium content, with the acid-precipitated casein containing 0.15% calcium and the centrifuged casein containing 2.87% calcium. Both caseins sorbed more water than the whey, the amounts being approximately of the same magnitude as that sorbed by milk powder up to  $0.5 P_0$ , the break-point in the milk powder isotherm.

#### Discussion

The sorption isotherms for lyophilized skim-milk and whey are similar in shape to those reported earlier for spray-dried products (1, 10, 12). Of interest are the weight maxima present in these isotherms which must be associated with some phase change occurring in the sorbent. Supplee (10) associated this behavior with some change in the protein fraction. However, Troy and Sharp (12) and most later workers have associated the discontinuity with lactose crystallization (9). In a previous communication (1) we demonstrated that the break in the isotherm results from lactose crystallization, as the amount of water desorbed at the breakpoint is inversely related to the amount of lactose present in the powder in crystalline

form. This view is substantiated with results we are reporting now for lactose-free milk and for pure lactose. The absence of any break in the isotherm for lactose-free milk powder and the very sharp maximum obtained with pure lactose clearly demonstrate that lactose crystallization is the sole cause of the break usually observed in the water sorption isotherms for dehydrated dairy products.

It is significant that the break in the lactose isotherm occurs at  $P/P_0 = 0.35$ ; whereas, with milk and whey powders it does not occur until at least a relative pressure of 0.5 is reached. It is likely that this shift in position of the maximum may be related to a lowered surface concentration of lactose in the milk powders, with the initial sorption site being some component other than the lactose glass.

To gain insight into the nature of the specific sites responsible for water binding in milk powders, we have taken our data for lactose, anhydrous Jenness-Koops salt mixture, and centrifuged casein, together with Bull's (3) data for  $\beta$ -lactoglobulin, and constructed the composite absorption isotherm shown in Fig. 5. The isotherm for the centrifuged casein was chosen due to its greater similarity to that of the skim-milk as compared with the acid-precipitated casein. This may be owing to the centrifuged casein being present in the micellar form before drying, as was the skim-milk. This is supported by the results of the calcium analyses.

Good agreement between the actual isotherm and the constructed one is observed only at low and high relative pressures. At intermediate relative pressures there is less agreement, because the phase transitions occurring in the lactose make it difficult to predict the exact position at which the break in the isotherm should occur.

Nevertheless, it is apparent from the calculated composite isotherm that water sorption

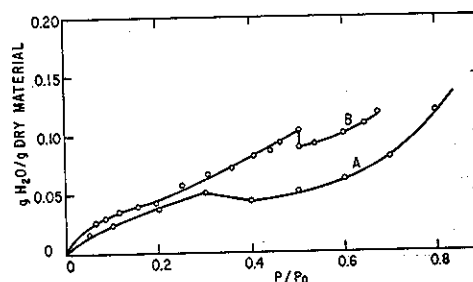


FIG. 5. Comparison of calculated water sorption isotherm for powdered skim-milk, A, with experimental isotherm for powdered skim-milk, B.

by the individual milk powder components is additive. Comparison of the mass sorbed by the individual constituents (Fig. 3 and 4) also permits us to state that water vapor sorption by milk powder occurs through a sequence of sorption sites as determined by the relative pressure.

At low relative pressure, water is preferentially bound by casein. As the water content of the milk powders increases, in atmospheres of increasing pressure, lactose binds water more strongly and acquires sufficient moisture to undergo a phase transition. At relative pressures above 0.5 the salts bind sufficient water to set the conditions for protein destabilization, as described by Fox et al. (5).

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